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Thermoluminescent Kinetics of Alpha-Irradiated Alkali Halides

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The kinetics of the thermoluminescence of single crystal NaCl, KCl, and KBr irradiated with 40-MeV alpha particles were investigated. Only one glow peak, composed essentially of a single emission band, was obtained for each of the salts investigated. To attempt complete analysis of the kinetics, both glow curve and isothermal annealing experiments were employed. The results from glow curves were shown to be unreliable for calculation of the kinetic order in the case of NaCl and KBr. The isothermal tests indicate the kinetics of the dominant process for NaCl to be first order; for KBr, first order; and for KCl, $\frac{2}{3}$ order. No general statement can be made concerning the order of these processes; thus, at present, the kinetics for each salt investigated must be determined individually. Occasionally, secondary processes occur in specimens of NaCl and KBr, even though essentially only one spectral peak was detected. A simple model for luminescence will explain the kinetics of NaCl and KBr; it involves activation of electrons from traps into the conduction band. To explain the results for KCl, a more complex model is required. Activation energies were also calculated.

author

INTRODUCTION

IN the study of the thermoluminescence of radiation-colored alkali halides, knowledge of the kinetic order can be helpful in forming the basis for a model used to explain the luminescent process. Over the years, however, only a few investigations of this nature have been reported for the alkali halides. Hill and Schwed[1] assume, without apparent experimental verification, that the thermoluminescence of x-irradiated NaCl is first order. Lushchik[2] makes a similar assumption presuming the absence of appreciable retrapping. However, Bonfiglioli *et al.*[3] assume such a process should be second order based on a different model. Finally, Halperin *et al.*[4] conclude that the thermoluminescence of NaCl is essentially a first-order process with a slight contribution of one of higher order. Halperin's results are based on glow-curve analyses of x-irradiated specimens. None of the above investigators was primarily interested in the determination of kinetic order *per se*; evaluation of activation energy was of more concern to them. Whether the kinetics are a function of the type

of irradiation used is not known since the kinetics of the thermoluminescence of NaCl, KCl, and KBr caused by particle irradiation has not been previously investigated.

Several factors should be considered in a preliminary investigation of the kinetics for thermoluminescent processes. First, the analysis can most easily be applied to well-isolated glow curves since overlap from neighboring curves can disturb intensity values. Second, the spectral composition of the light emitted should be simple in order to minimize the possibility of concurrence of two or more interdependent processes. Furthermore, the entire concept of kinetic order could lose its meaning in a kinetic process complicated by either multiple glow curves or multiple spectral peaks.

In the present investigation, the glow curves of each of the three salts consisted of only one glow peak composed essentially of a single emission band; thus, difficulties arising from the above-mentioned factors should be minimized. For NaCl, a slight shoulder on the emission band may indicate the presence of a second band; no shoulders were detectable on the emission band for either KBr or KCl.

This paper describes the determination of the kinetic order for the thermoluminescent processes using two distinct methods. The first, isothermal annealing, allows

[1] J. J. Hill and P. Schwed, J. Chem. Phys. **23**, 652 (1955).
[2] C. B. Lushchik, Dokl. Akad. Nauk, SSSR **101**, 641 (1955).
[3] G. Bonfiglioli, P. Brovetta, and C. Cortese, Phys. Rev. **114**, 951 (1959).
[4] A. Halperin, A. A. Braner, A. Ben-Zvi, and N. Kristionpoller, Phys. Rev. **117**, 416 (1960).
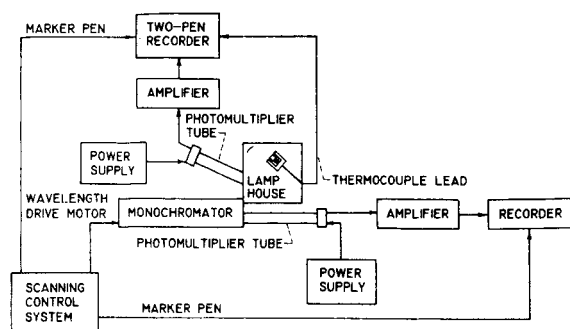
FIG. 1. Schematic diagram of recording apparatus.

the light emission from the crystal to occur at a constant temperature. The advantage of this method is that the mathematical treatment requires the use of only a few variables. The second method utilizes the glow curve produced by annealing the crystal at a constant heating rate. This method has the advantage of experimental convenience and allows activation energies to be calculated readily, which in part accounts for its widespread use for trap-depth studies.[1-4] Finally, models were set up in keeping with the kinetic order determined.

EXPERIMENTAL

Single crystals of NaCl, KCl, and KBr were obtained from the Harshaw Chemical Company in the form of 1 in. diam disks, 2 to 3 mm thick. Crystals of one particular salt were not necessarily from the same ingot, since the crystals were purchased at various times. Some crystals were used as received, while a slightly smaller number were heat treated in a nitrogen atmosphere for 24 h at 720°C. The irradiations were performed with the specimens at room temperature using 40-MeV alpha particles from the NASA 60 in. cyclotron. The beam current was kept low so that heating of the crystal was slight and could be ignored. The total flux on every crystal was approximately 10^{14} particles per cm². After irradiation, the disks were cleaved to convenient size for analysis.

The apparatus is shown schematically in Fig. 1, and is described elsewhere.[5] In short, it recorded simultaneously the glow curves, the spectral components, and the temperature of the furnace. The spectrum scanned was from 300 to 700 mμ at the rate of about 25 mμ/sec using the monochromator and wavelength drive from a Beckman DK–1 spectrophotometer. The lamphouse was modified so that a small crystal heating furnace replaced the tungsten lamp normally used as the light source. The furnace could be heated uniformly from 40° to 300°C at the rate of 0.76°C per sec. By this method about 20 glow-curve measurements were performed on each of the three salts.

[5] J. A. Partridge, "Thermoluminescent Spectra of Sodium Chloride and Hydroxide Free Sodium Chloride Irradiated with 40-MeV Alpha Particles," NASA TN D–1662 (1963).

Isothermal decay curves were taken using the same apparatus, but the furnace was maintained at a constant temperature near that of the glow peak for the type of crystal to be analyzed. The specimen was placed into the preheated furnace. The assumption was made that the crystal had come to thermal equilibrium shortly after the light output had passed a maximum; the experimental results verify that this was essentially true. About 30 isothermal decay curves were measured for each of the three salts.

Typical glow and isothermal decay curves for KCl are shown in Fig. 2; the intensity values given in this and subsequent figures are all in arbitrary units. The curves for NaCl and KBr are roughly similar to those in Fig. 2. Other data are tabulated in Table I. For each
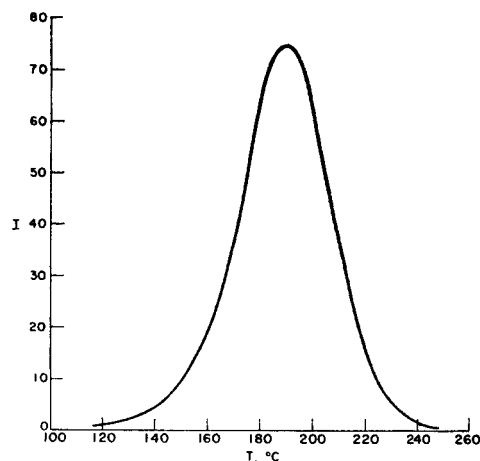
(a)
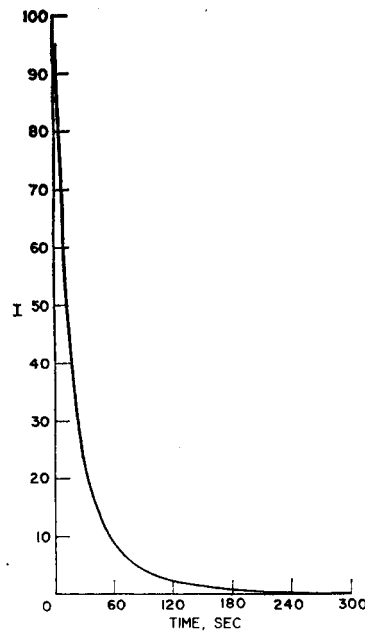
(b)

FIG. 2. (a) Typical KCl data: glow curve. (b) Concluded. Typical KCl data: isothermal decay; $T = 202°C$.

of the salts, the wavelength of the spectral peak for the isothermal decay curves was the same as that for the glow curves.

RESULTS AND DISCUSSION

Isothermal Luminescence

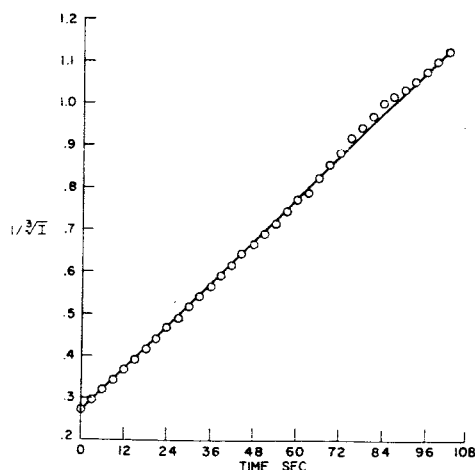In many cases the kinetics of the luminescent should be expressible as follows[1]:

$$I = \gamma C^n e^{-E/kT}, \qquad (1)$$

where I is the intensity of light at anytime, γ a proportionality constant, C the concentration of filled traps, E the activation energy, T the absolute temperature, n the order of reaction, and k the Boltzmann constant. For a first-order isothermal reaction, the log I plotted against time should yield a straight line. For other than first order, the plot $I^{(1/n-1)}$ vs time should be a straight line. The validity of such plots can be shown by the combination of Eq. (1) and the integrated form of $dC/dt = -(\gamma/\epsilon)C^n e^{-E/kT}$ through the elimination of C, assuming the temperature to be constant.
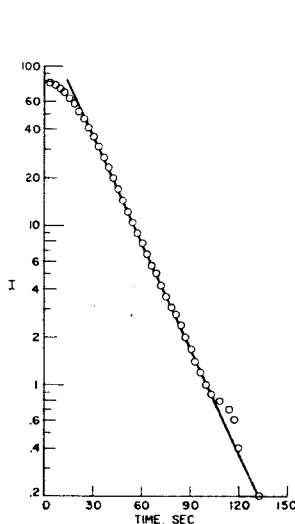
The kinetic process for KCl is shown to be 3/2 order by a plot of $I^{-1/3}$ vs t [Fig. 3(a)]. For KBr and NaCl the majority of the data indicates first order [Figs. 3(b) and 3(c)]; in fact, all the data indicate first order, at least for part of the time, as seen in Figs. 4 and 5. These figures show that the kinetics begin as first order and then deviate from it after a short time; this deviation may be due to the introduction of a secondary mechanism or process. The dominant process appears to be first order for both NaCl and KBr. For the NaCl, the secondary process may also be first order, since the last part of the curve (Fig. 4) is also a straight line, and the actual intensity curve can be interpreted as the sum of two concurrent intensities, as indicated by the two dotted lines, and as expressed by the following equation:

$$I = \gamma_x C_x e^{-E_x/kT} + \gamma_y C_y e^{-E_y/kT} \quad \text{(first order only)}, \quad (2)$$
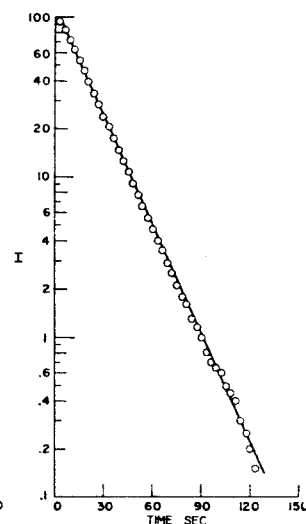
where the x and y designate the two processes involved. Due to the second inflection point in Fig. 5 the secondary process for KBr cannot be as simple as that for NaCl. Resolution of this curve into two components is not unique; one of many possible resolutions is shown by the dotted lines (Fig. 5). Such a resolution

TABLE I. Glow-curve data.

Crystal	Temperature of glow peak (°K)	Wavelength of spectral peak (mμ)	Activation energy (eV)
NaCl	535	360	1.82
KCl	460	440	1.38
KBr	500	435	1.5

FIG. 3. (a) Analysis of isothermal decay: KCl as $\frac{3}{2}$'s order; $T = 223°C$. (b) Analysis of isothermal decay: NaCl as first order, $T = 272°C$. (c) Concluded. Analysis of isothermal decay: KBr as first order; $T = 219°C$.

would suggest an induction period for the secondary process. It should be noted that essentially a single spectral peak (Table I) was detected for each specimen, even though some of the specimens of NaCl and KBr involved apparently two processes.

An alternate method of analysis (Appendix A) for the isothermal data yields the same results.

It should be mentioned that two specimens cleaved from the same irradiated sample of NaCl or KBr would many times vary in their luminescent behavior. One specimen would show a single first-order process, while the other would show, in addition, a secondary process. Thus, the slight differences in behavior can neither be attributed to differences in pretreatments of the samples nor to variations between batches during the manufacture. Perhaps, the differences are caused by local variation of the impurity content.
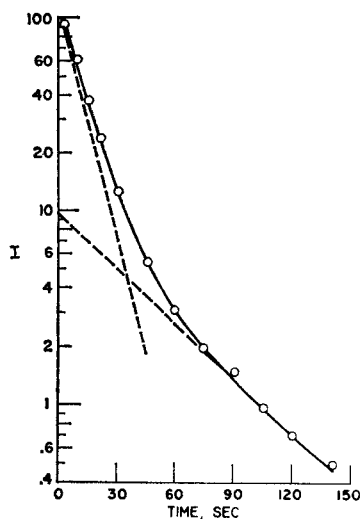
FIG. 4. Isothermal decay of NaCl showing two concurrent processes; solid line represents experimental data; dotted lines show resolution into two processes; $T = 272°C$.

FIG. 6. Analysis of KCl glow curve.

Glow Curves

If Eq. (1) is again assumed to be applicable, the kinetic order may likewise be obtained from glow-curve data. Determination of n requires a series of plots of $\log I/C^n$ vs $1/T$, where

$$C = \frac{1}{\epsilon}\int_{t_T}^{\infty} I dt \qquad (3)$$

(t being time, t_T being the t corresponding to T, and ϵ being an arbitrary proportionality constant), since
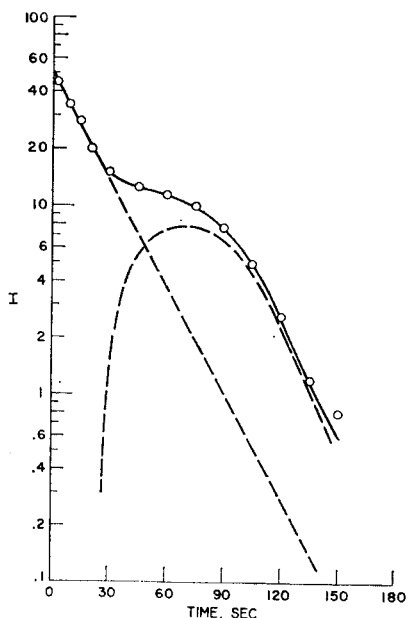
$$I = -\epsilon(dC/dT). \qquad (4)$$

FIG. 5. Isothermal decay of KBr showing two concurrent processes; solid line represents experimental data; dotted lines show resolution into two processes; $T = 216°C$.

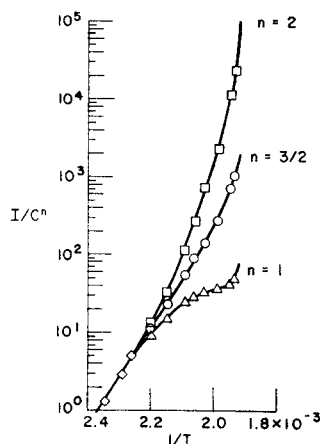By visual examination of such plots, the value of n which gives the best straight line can be ascertained; this value of n can be interpreted as the kinetic order. The activation energy is obtainable from the slope of the line. It should be noted that the application of the above equations does not require the use of a constant heating rate; however, a constant heating rate does facilitate the processing of the data.

The data from the samples of KCl are quite good. With few exceptions, the KCl data fit 3/2-order kinetics as shown in Fig. 6. Even the exceptions fit a 3/2-order plot by using two straight-line portions (Fig. 7). The higher-temperature portion has the same slope (and thus activation energy) as the curves indicating 3/2 order (Fig. 6). This suggests that the kinetic order may change with temperature, and that in a few specimens 3/2-order kinetics were operative only at the higher temperature. The kinetic order in the lower-temperature region (Fig. 7) cannot be ascertained, since the fit of the lower portion of the curve is not sensitive to the value of n used. However, its slope (activation
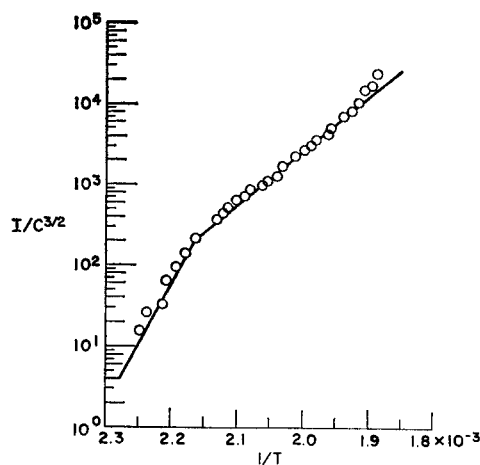

FIG. 7. Analysis of KCl glow curve as $\frac{3}{2}$'s order.

energy) appears to be about twice that of the curves indicating 3/2-order kinetics.

The glow-curve data for both NaCl and KBr are very conflicting. The reason for this is discussed in the following section. Most of the data for NaCl appear to show second-order kinetics, although the fit is very poor (Fig. 8). For some of the NaCl data no reasonable fit at all can be obtained regardless of the kinetic order assumed; in a few cases, first order is indicated. The results for the KBr are essentially the same as for the NaCl, although the fit is a little better. Again, most of the data indicate second-order kinetics [Fig. 9(a)]; some show first order [Fig. (9b)]; and for the remaining data no reasonable fit at all is obtainable.

Comparison of the Two Methods

It is obvious after a comparison of the last two sections that, in general, the two experimental methods are not in agreement. If the luminescence consists of a single kinetic process, the methods would normally be expected to agree with one another. For KCl a single process seems to occur, and, indeed, both methods indicate 3/2 order. However, for NaCl and KBr, the isothermal data indicate that more than one process can sometimes occur. Each such process may well have its own activation energy; under this condition Eq. (1) cannot be applied, and application of the more general Eq. (2) is extremely difficult under nonisothermal conditions. Thus, in the present case, the isothermal tests should be used as the criteria for the kinetic order. Hence, the dominant thermoluminescent process for both alpha-irradiated NaCl and KBr is concluded to be first order. The fact that some of the specimens appeared to show second-order kinetics in glow-curve experiments is possibly an accidental result of the combination of secondary processes.

It should be noted that a simple process may appear to be first order in isothermal tests and second order
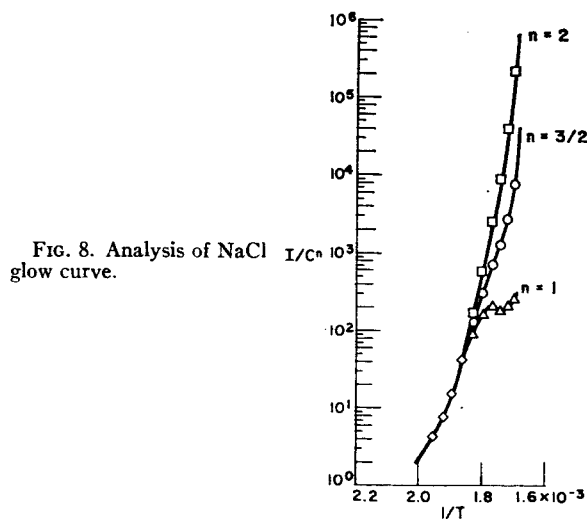

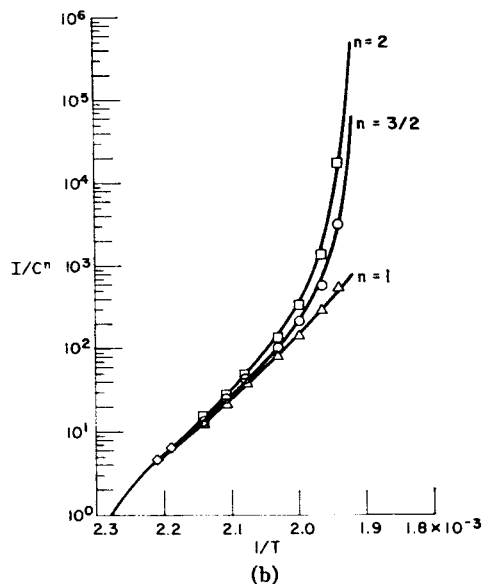FIG. 8. Analysis of NaCl glow curve.

(a)

(b)
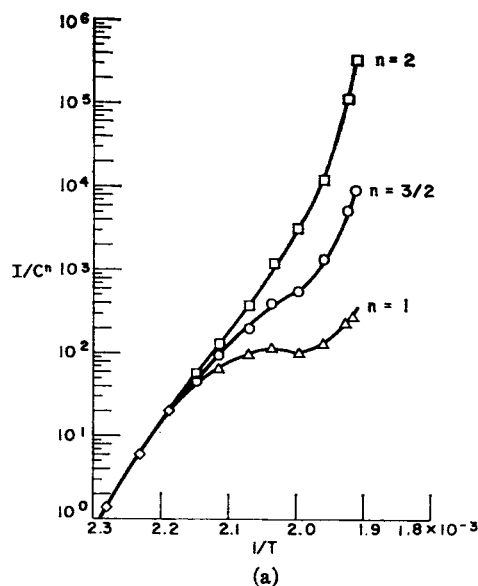
FIG. 9. (a) Analysis of KBr glow curve showing second order. (b) Concluded. Analysis of KBr glow curve showing first order.

in glow-curve determinations, if the heating rate is sufficiently great; this is probably not the situation in the present investigation. (See Appendix B.)

Activation Energy

Although the glow-curve analysis in the present investigation does not always give the proper value for the kinetic order of the process involved, it is useful in obtaining activation energies [Eq. (1)]. The values given in Table I for NaCl and KBr are the average of those obtained from glow curves indicating first-order kinetics. Values obtained from curves indicating second-order processes for NaCl and KBr were higher

CONDUCTION BAND

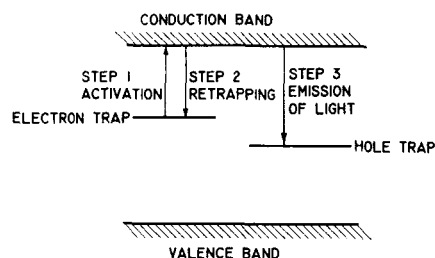| STEP 1 ACTIVATION | STEP 2 RETRAPPING | STEP 3 EMISSION OF LIGHT |

ELECTRON TRAP

HOLE TRAP

VALENCE BAND

FIG. 10. Model of process.

and were not deemed reliable due to the presence of concurrent processes. The average value obtained for the activation energy for the KCl process is also given in Table I.

In many chemical processes the activation energy can be obtained from a series of isothermal reactions carried on at various temperatures. In the thermoluminescent processes reported here the temperature range usable for isothermal tests was only about 30°C and thus did not allow reliable calculations of activation energy to be made.

Model for NaCl

A process of thermoluminescence which consists of an isolated glow peak composed of a single emission band could be explainable by the familiar model[6-8] consisting of a single type of electron trap and a single type of hole trap as shown in Fig. 10. One possible mechanism consists of the thermal activation of an electron from a trap to the conduction band,[9] followed by its combination with a hole or luminescent center, resulting in the emission of light. Also to be considered is the retrapping process illustrated in Fig. 10.

The general equation applicable to this model has been derived by many authors assuming steady-state conditions. The one presented here is essentially that of Hoogstraaten[10] and is a special case of the one derived in Appendix B.

$$I = \gamma_1\gamma_3 C^2 e^{-E/kT} / [\gamma_2 H + (\gamma_3 - \gamma_2)C], \quad (5)$$

where γ_1, γ_2, and γ_3 are rate constants for the activation, retrapping, and emission, respectively, and H is the total concentration of electron traps, both filled and empty. The intensity can be expressed as a function of time rather than as a function of C, but this equation is much more complex.[11]

[6] S. F. J. Garlick, "Luminescence," in *Encyclopedia of Physics*, (Springer-Verlag, Berlin, 1958), Vol. 26, I p. 66.
[7] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 366 (1945).
[8] A. Halperin and A. A. Braner, Phys. Rev. 117, 408 (1960).
[9] The present data does not eliminate the possibility that the activation step involves the movement of a hole from its trap to the valence band; however, the majority of the literature indicates that it is the activation of the electron which takes place in such a process.
[10] W. Hoogstraaten, Philips Res. Repts. 13, 515, 1958, (Eq. 4.1).
[11] H. A. Klasens and M. E. Wise, Nature 158, 483, 1946 (Eq. 11).

It is easily seen that when

$$(\gamma_3 - \gamma_2)C \gg \gamma_2 H$$

the kinetics will be first order as is found for NaCl in this investigation. Such a process leaves the activation step as rate controlling. However, as C decreases, the process would slowly convert to a second-order process. Equation (5) can be rearranged so that such a conversion can be more easily checked experimentally.

$$(\gamma_2 H/C) + \gamma_3 - \gamma_2 = \gamma_1\gamma_3 Ce^{-E/kT}/I \quad (6)$$

A plot of C/I vs $1/C$ should result in a straight line if there is a tendency for first-order kinetics to transform to second order. Indeed, such plots for some of the data for NaCl indicate that this type of transition sometimes does exist (Fig. 11).

In general, however, the model for the thermoluminescence of NaCl is that depicted in Fig. 10, with the activation being the rate-controlling step. Occasionally the presence of a second electron trap might be required in order to explain the auxiliary first-order process indicated in Fig. 4. Plots of glow curves for double processes, or ones complexed by partial conversion to a second-order process, cannot be expected to result in well-fitted straight lines (Fig. 8).

Model for KBr

The general model for KBr is the same as for NaCl (Fig. 10). Again a second filled electron trap is needed to explain the auxiliary process indicated in Fig. 5. The data do not allow one to ascertain the kinetics of this secondary process. As mentioned before, the existance of such a secondary process hinders one from proper interpretation of glow curves; thus, poor fit with glow curves is expected, and the order of reaction thus obtainable would be variable and unreliable.
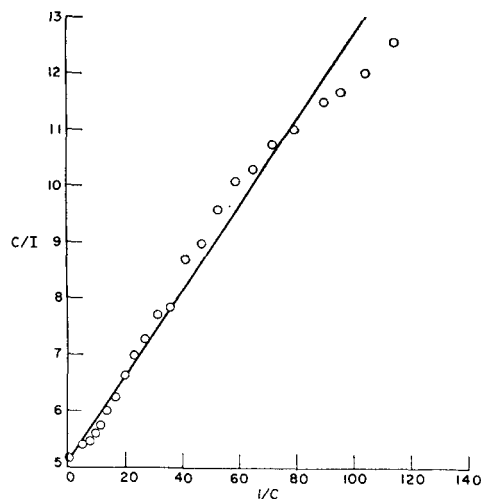

FIG. 11. Isothermal decay of NaCl indicating transformation of kinetic order; $T = 278°C$.

Model for KCl

The interesting results obtained from KCl requires that we modify the model of Fig. 10. The only satisfactory modification we could devise was one in which the electron trap contains two electrons that are simultaneously activated to the conduction band. This is, of course, a rather unusual condition, but lacking further information we present this model as a tentative explanation. The applicable equation for the isothermal case is derived in Appendix C.

$$I = \frac{\gamma_3^2 C^2}{2\gamma_2(H-C)} \left\{ \left[\frac{4\gamma_1\gamma_2(H-C)e^{-E/kT}}{\gamma_3 C} \right]^{\frac{1}{2}} - 1 \right\}, \quad (7)$$

where E is the activation energy for the electron pair. If C is large, the process approaches first-order kinetics.

$$I = \gamma_1 C e^{-E/kT}. \quad (8)$$

If, however, C is small, the process approaches 3/2-order kinetics.

$$I = \gamma_3(\gamma_1/\gamma_2 H)^{\frac{1}{2}} C^{3/2} e^{-E/kT}. \quad (9)$$

All of the isothermal tests and most of the glow curves follow 3/2 order, substantiating this model and indicating that the emission step is the rate-controlling step. Since the luminescent reaction in the case of KCl appears to be a single process, it is not unusual that the data from glow curves are interpretable. It is interesting to note that even the double-sloped curves (Fig. 7) are explainable. In the higher-temperature region C is small, and thus the normal kinetics are observed along with the proper activation energy. However, in the lower-temperature regions C is larger, and first-order kinetics might be operating [Eq. (8)] with an activation energy (slope) twice that of the 3/2 kinetic process; one finds that the low-temperature slope in Fig. 7 is about twice the high-temperature slope. As mentioned before, the order of the low-temperature process cannot be determined from the curve; it can only be inferred.

CONCLUDING REMARKS

The kinetic orders found for the three salts investigated are the results from commercial samples irradiated with 40-MeV alpha particles. The same results may not necessarily be obtained using specimens irradiated with x-rays, or with other particles (electrons, protons, etc.), or even with different flux levels and specimen temperatures. However, it should be noted that both this investigation using alpha irradiation and Halperin's investigation[4] using x-irradiation result in an essentially first-order thermoluminescence for NaCl. The kinetic order might also be influenced by impurities in the commercial samples[12]; in fact, impurity states may actually be participating in the thermoluminescent processes investigated.

[12] Preliminary kinetic studies show that specimens of KCl from Semi-Elements behave similar to those from Harshaw; however, KCl from Optovac exhibits a more complex behavior.

However, this research does point out that the kinetic order can vary for thermoluminescence from one alkali halide to another; it can be first or 3/2-order. Moreover, even a second-order process is possible (Fig. 11). Therefore, one should not *a priori* make an assumption concerning the kinetics of such a process. In addition, unless the process being investigated is experimentally proven to be simple, care should be used in the interpretation of kinetic order, expecially when obtained from glow-curve data.

APPENDIX A

ALTERNATE ISOTHERMAL ANALYSIS

An alternate method of analysis for isothermal luminescence consists of plotting $\log(-dI/dt)$ against $\log I$. The kinetic order can be determined from the slope, S, of the resulting straight line from the relationship, $n = 1/(2-S)$. The value of this method is that it does not involve trial and error. Its validity can be simply shown by means of the following derivation. By differentiation of Eq. (1) at constant T, followed by substitution of Eq. (3), we obtain

$$\frac{dI}{dt} = n\gamma C^{n-1} e^{-E/kT} \left(\frac{dC}{dt} \right) = \frac{-n\gamma}{\epsilon} C^{n-1} e^{-E/kT} I. \quad (A1)$$

Upon elimination of C between Eqs. (1) and (A1),

$$\frac{dI}{dt} = \frac{-n\gamma^{1/n}}{\epsilon} e^{-E/nkT} I^{(2-1/n)}. \quad (A2)$$

Rearrangement yields the desired equation:

$$\log\left(-\frac{dI}{dt} \right) = \left(2 - \frac{1}{n} \right) \log I - \frac{2.303E}{nkT} \log\left(\frac{n\gamma^{1/n}}{\epsilon} \right). \quad (A3)$$

The isothermal data for NaCl, KCl, and KBr were plotted in this manner; most of the data resulted in straight-line plots. The orders of reaction indicated are: first for NaCl, 3/2 for KCl, and first for KBr. The few examples for NaCl and KBr which did not result in straight-line plots were those consisting of two concurrent processes.

APPENDIX B

KINETICS FOR A CONSTANT HEATING-RATE PROCESS

In the model (Fig. 10) the process is considered to consist of three steps:

Activation,

$$r_1 = \gamma_1' QC e^{-E/kT}; \quad (B1)$$

Retrapping,

$$r_2 = \gamma_2 m(H-C); \quad (B2)$$

Light emission,

$$r_3 = \gamma_3 mC; \quad (B3)$$

where r_1, r_2, r_3 are the rates for the three steps involved, Q is the total concentration of states in the conduction

band, m is the concentration of electrons in the conduction band, H is the total concentration of electron traps (both filled and empty), C is the concentration of filled electron traps as well as hole traps (the two being equal if only one type of each exists), and γ_1', γ_2, γ_3 are the transition probabilities. For simplicity we define: $\gamma_1 = Q\gamma_1'$.

In most kinetic derivations, a steady-state process is assumed, that is,

$$dm/dt = 0 = r_1 - r_2 - r_3. \qquad (B4)$$

This is a reasonable assumption for a constant temperature process, but perhaps not for one of constant heating rate, α, where $T = T_0 + \alpha t$. However, a constant heating rate condition can easily be taken into consideration by first introducing a quantity F defined by the following equation:

$$m = Fe^{-E/kT}. \qquad (B5)$$

From an examination of Fig. 10, followed by substitutions using Eqs. (B1), (B2), (B3),

$$dm/dt = r_1 - r_2 - r_3 = \gamma_1 Ce^{-E/kT} - \gamma_2 m(H-C) - \gamma_3 mC \neq 0. \qquad (B6)$$

With substitutions for the values of m and t,

$$-\frac{d(Fe^{-E/kT})}{d(1/T)}$$

$$= \frac{T^2}{\alpha}[\gamma_1 Ce^{-E/kT} - \gamma_2 H Fe^{-E/kT} + (\gamma_2 - \gamma_3)CFe^{-E/kT}]. \qquad (B7)$$

Upon simplifying,

$$-\frac{dF}{d(1/T)} + \frac{EF}{k} = \frac{T^2}{\alpha}[\gamma_1 C - \gamma_2 HF + (\gamma_3 - \gamma_2)CF]. \qquad (B8)$$

Rough numerical evaluation shows that EF/k has a magnitude of about 20 times that of

$$\frac{dF}{d(1/T)},$$

so that the derivative can be deleted:

$$F = \gamma_1 / (E\alpha/CkT^2 + \gamma_2 H/C + \gamma_3 - \gamma_2). \qquad (B9)$$

Since r_3 is the emission step,

$$I = r_3 = \gamma_3 FCe^{-E/kT}. \qquad (B10)$$

Therefore,

$$I = \gamma_1 \gamma_3 C^2 e^{-E/kT} / [E\alpha/kT^2 + \gamma_2 H + (\gamma_3 - \gamma_2)C]. \qquad (B11)$$

For small values of α the equation degenerates into steady-state conditions [Eq. (5)]. For relatively large values of α, the terms $\gamma_2 H$ and $(\gamma_3 - \gamma_2)C$ may become insignificant, and the equation reduces to apparent second-order kinetics.

$$I = (\gamma_1 \gamma_3 kT^2 C^2 / E\alpha)e^{-E/kT}. \qquad (B12)$$

The numerical value of $E\alpha/kT^2$ is approximately 10^{-2}/sec in the present investigation; however, the values for $\gamma_2 H$, $\gamma_2 C$, and $\gamma_3 C$ are not as readily calculated. The dominant term of these three is probably $\gamma_3 C$, which should correspond to the transition probability for an emission process. For a dipole transition, which is likely the situation in the present investigation, the value should be about 10^6/sec; thus, the heating rate effect can likely be ignored. If one is concerned with a multiple transition, the value of $\gamma_3 C$ might be as low as 10^{-5}/sec; thus, the heating rate effect would be important, and the glow-curves process would appear to be second order while the isothermal process is first order.

A further comment should also be made; when the kinetics reduce to first order, the concentrations of the filled electron traps and the hole traps are no longer required to be equal for proper application of the equation. The only concentration involved is that of the filled electron traps.

APPENDIX C

KINETICS INVOLVING THE SIMULTANEOUS ACTIVATION OF TWO ELECTRONS

Figure 10 can also be used to describe the thermoluminescent process for KCl. In this case two electrons would be contained in what could be called a single trap; thus two electrons, however, may be located in a single lattice site or in two sites of very close proximity. The activation process would consist of excitation of both electrons simultaneously into the activated state. The applicable rate equations differ somewhat from Eqs. (B1), (B2), and (B3):

$$r_1 = \gamma_1 Ce^{-E/kT}, \qquad (C1)$$

$$r_2 = \gamma_2 m^2(H-C), \qquad (C2)$$

$$r_3 = \gamma_3 mC, \qquad (C3)$$

where E is the activation energy for two electrons and the other symbols have essentially the same meaning as in Appendix B. Under steady-state conditions,

$$dm/dt = 0 = r_1 - r_2 - r_3 = \gamma_1 Ce^{-E/kT}$$
$$- \gamma_2 m^2(H-C) - \gamma_3 mC. \qquad (C4)$$

Solving for m,

$$m = \frac{\gamma_3 C}{2\gamma_2(H-C)}\left\{\left[\frac{4\gamma_2(H-C)\gamma_1}{\gamma_3^2 C}e^{-E/kT}\right]^{\frac{1}{2}} - 1\right\}. \qquad (C5)$$

Since r_3 is the emission step,

$$I = r_3 = \gamma_3 mC = \frac{\gamma_3^2 C^2}{2\gamma_2(H-C)}\left\{\left[\frac{4\gamma_2(H-C)\gamma_1}{\gamma_3^2 C}e^{-E/kT}\right]^{\frac{1}{2}} - 1\right\}. \qquad (C6)$$

When

$$4\gamma_2\gamma_1 e^{-E/kT}/\gamma_3 C \ll 1,$$

we obtain

$$I = \gamma_1 C e^{-E/kT}, \tag{C7}$$

which is the situation when the activation process is the rate controlling step.

However, when

$$4\gamma_2\gamma_1 e^{-E/kT}/\gamma_3 C \gg 1,$$

we obtain

$$I = C^{3/2}[\gamma_1\gamma_3/\gamma_2(H-C)]e^{-E/2kT}, \tag{C8}$$

which is the situation when the emission process is the rate controlling step. If, in addition, [for Eq. (C8)] $C \ll H$, 3/2-order kinetics should be exhibited and this model becomes useful in explaining the thermoluminescent kinetics for KCl.

The kinetics of this model have also been derived assuming a constant heating rate process; the resultant equation is, of course, more complex. When the heating rate is relatively small, the equation simplifies into Eq. (C6). If the heating rate is relatively large, a second-order equation results.